Novel ruthenium(II) and zinc(II) complexes for two-photon absorption related applications

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Received 4th May 2007, Accepted 18th May 2007 First published as an Advance Article on the web 20th June 2006 DOI: 10.1039/b706715a

Two new fluorene derivatized 1,10-phenanthroline ligands and related tris-chelate Ru(II) or Zn(II) coordination complexes have been synthesised. The linear and nonlinear (two-photon induced fluorescence) photophysical measurements have contributed to highlight the possibility to tune the absorption spectral range and excited lifetime, depending on ligand substitution and nature of the metal. More significantly, the observation of two-photon absorption (TPA) associated with long-lived metal-to-ligand charge-transfer (MLCT) excited states in the Ru(II)-based chromophores, opens a wide range of applications in the near infrared.

Introduction

Owing to its wide-ranging applications¹ (photodynamic therapy,² photochemical delivery of biological messenger,3 confocal microscopy,⁴ three dimensional data storage,⁵ microfabrication⁶ and optical power limiting⁷), the two-photon absorption (TPA) process, is a very attractive third order nonlinear optics (NLO) effect. In this field, coordination complexes8 have received less interest than organic chromophores,9 in spite of indisputable advantages: synthetic tailorability¹⁰ and the possibility of long luminescence lifetime of the MLCT (metal-to-ligand charge transfer) triplet excited state (a few microseconds are generally obtained for Ru(II) complexes for example^{11,12}). The access via TPA to the ³MLCT state could therefore generate interesting properties in fluorescence based effects (two-photon excited fluorescence, TPEF) such as biological imaging or O₂ sensing,¹³ and in processes involving excited state re-absorption such as optical power limiting.¹⁴ In this context, the high stability and inertia in solution of Ru(II) complexes allow their utilization in practical applications. To the best of our knowledge, only a few studies were carried out on MLCT transitions by TPA at a single wavelength (750, 800 and 880 nm) for ruthenium(II)¹⁵ and rhenium(I)¹⁶ complexes or Z-scan experiments giving rise to two-photon transitions spectra.¹⁷

Concerning the luminescence of the ³MLCT state and as in the case of the linear absorption, the TPEF of Ru(II) complexes involves the excitation of either singlet excited states of the ligand or the ¹MLCT state. Therefore, TPA properties of ruthenium complexes will be closely related to those of ligands and the optimisation of these latter is a relevant step. In this context, this paper deals with the synthesis and TPA properties of new ruthenium complexes C1 and C2 (see Fig. 1 later), in comparison with those of corresponding 5-oligofluorene-1,10-phenanthroline type ligands and related Zn complexes. The choice of ligands L1 and L2, bearing a fluorene or a bifluorene for C1 and C2 respectively, was based on TPA properties of oligofluorenes that we have recently ascribed to excitonic coupling between neighbor monomers.¹⁸ In the spectral range 700–940 nm and in order to identify unambiguously the MLCT transition through two-photon process, the properties of Zn complexes (C'1 and C'2) have been studied in comparison with those of Ru complexes. Due to the high ionisation potential of this metal, they should not present any MLCT type transition.

Results and discussion

Ligands L1 and L2 were prepared according to a Suzuki crosscoupling reaction starting from 5-bromo-1,10-phenanthroline¹⁹ and already described²⁰ boronic acid 2 and 3, respectively (see Scheme 1). Related ruthenium and zinc complexes (see Fig. 1) were obtained by reaction under reflux of three equivalents of ligand with one equivalent of either ruthenium trichloride (in dimethylformamide) or zinc acetate (in ethanol), respectively and precipited by NH₄PF₆. All systems were fully characterized by



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Fig. 1 Ru (Zn) complexes C1 (C'1) and C2 (C'2) involving ligands L1 and L2, respectively (general atom numbering also given for NMR description).

NMR, elementary analysis and mass spectroscopy (see experimental part).

Absorption spectra of complexes C1 (C2) and C'1 (C'2) are displayed in Fig. 2 (Fig. 3), in comparison with those of related ligands L1 (L2); maximum wavelengths are reported in Table 1. Three types of bands were observed in these complexes : (i) a band lying in the range 260–270 nm, (ii) a band pointing at 330 (305) and 335 (330) nm for C1 (C'1) and C2 (C'2), respectively, (iii) a group of bands between 410 and 460 nm for C1 and C2 only. The



Fig. 2 Absorption and normalised luminescence spectra at room temperature of ligands L1 and related Ru (C1) and Zn (C'1) complexes in acetonitrile.



Fig. 3 Absorption and luminescence spectra at room temperature of ligands L2 and related Ru (C2) and Zn (C2) complexes in acetonitrile.

two first bands were also observed in ligand L1 (L2) at 270 (265) and 310 (340) nm. Theoretical calculations on excited states of L1 and L2 allowed to determine the origin of these two bands. Theoretical linear maximum absorption wavelengths of L1 and L2 are reported in parentheses in Table 1; a satisfying agreement between experimental and calculated data was obtained. L1 and L2 present a theoretical absorption at 264 and 261 nm respectively, close to that of the phenanthroline calculated at 261 nm. The description of relevant orbitals involved in these transitions allowed to relate these latter mainly to the phenanthroline itself, as shown in Fig. 4 for L1, the transition calculated at 264 nm, which corresponds mainly to the excitation from the occupied HOMO-2 to the unoccupied LUMO, is only centered on the phenanthroline moiety. This confirms the attribution of these L1 and L2 bands.

Theoretical absorption bands of L1 and L2 at 287 and 294 nm, related to experimental transitions at 310 and 340 nm respectively, correspond to the excitation from the HOMO to the LUMO+1 for both bands, as shown in Fig. 5 in the case of L1, the HOMO is mainly localised on the fluorene, while the LUMO+1 is concentrated on the bipyridyl moiety, indicating the charge transfer (CT) character of this transition. The bathochromic shift of this transition between L1 and L2 in experimental and theoretical spectra is in good agreement with this CT origin.

All these bands still exist in Ru (C1, C2) and Zn (C'1, C'2) complexes : the phenanthroline band was observed at 266 and 267 nm in Ru complexes, and 270 and 265 nm in Zn analogs,

Table 1 Photophysical characteristics in acetonitrile of ligands L1 and L2, related Ru complexes C1 and C2, and Zn complexes C1 and C2

Compound	$\lambda_{abs}{}^{a}/nm$	$\varepsilon^b/L \text{ mol}^{-1} \text{ cm}^{-1}$	$\lambda_{\rm em}^{c}/{\rm nm}$	ϕ^{d}	τ^{e}/ns	$\lambda_{\text{TPA}}^{f}/\text{nm}$	$\sigma_{ ext{TPA}}{}^{g}/ ext{GM}$
L1 L2 C1 C2 C1	270 (264), 310 (287) 265 (261), 340 (294) 266, 330, 410–460 267, 335, 410–460 270, 305	40300, 25100 28000, 61300 156200, 49500, 30900 ^h 116600, 177300, 32100 ^h 137800, 69600	398 418 590 595 480	0.93 0.30 0.09 0.11 0.15	1.4 1.7 1700 2500 6.1	530 560 (488, 520sh) 740, 850, 930 750, 850, 930 595, 750	16 75 40, 15, 15 90, 15, 15 88, 10
C'2 [Ru(Phen) ₃](PF ₆) ₂	265, 330 262 (261), 440–460	81000, 134900 117400, 19300 ^h	590	0.0312	890	 750, 850, 930	20, 10, 10

^{*a*} λ_{abs} : one-photon absorption maximum wavelength (theoretical value in parentheses). ^{*b*} ε : molecular absorption coefficient at λ_{abs} . ^{*c*} λ_{cm} : emission maximum wavelength. ^{*d*} ϕ : fluorescence quantum yield determined relative to the MSB for organic compounds and to the Ru(bipy)₃(PF₆)₂ for ruthenium complexes. ^{*e*} τ : luminescence lifetime. ^{*f*} λ_{TPA} : maximum two-photon absorption wavelength. ^{*g*} σ_{TPA} : two-photon absorption cross-section, GM stands for Göppert–Mayer with 1 GM = 10⁻⁵⁰ cm⁴ s photon⁻¹. ^{*h*} Molar extinction coefficient at 440 nm, sh: shoulder.



Fig. 4 Representation of HOMO-2 (a) and LUMO+1 (b) of L1 orbitals mainly involved in the transition calculated at 264 nm.



Fig. 5 Representation of HOMO (a) and LUMO+1 (b) of L1 orbitals mainly involved in the transition calculated at 287 nm.

the usual intraligand charge transfer (ILCT) band is observed in Ru (C1, C2) and Zn (C'1, C'2) complexes with no significant wavelength shift with respect to parent ligand (the highest shift of 20 nm is observed in the case of C1). C1, C2, as $[Ru(Phen)_3](PF_6)_2$, present bands between 420 and 460 nm, which are ascribed to MLCT transitions between the Ru(II) d π and the ligand π^* orbitals. As expected, this type of transition is not observed in C'1 and C'2. The interest of these bands will be discussed below.

Luminescence spectra consist in broad bands centered at 590 and 595 nm for C1 and C2, respectively (see Table 1, Fig. 2 and Fig. 3). Related excitation spectra of these emissions, involving intraligand bands and MLCT (Fig. 6 for L1, C1 and C'1), are in good agreement with the emission from the ³MLCT state. This is also evidenced by the long luminescence lifetimes measured for C1 and C2 (1.7 and 2.5 μ s, respectively) as compared to those of the ligands (results gathered in Table 1). Let us stress that, although the introduction of a fluorene unit on each branch of the ligand does not induce a shift of the emission band for C1 and C2, it leads to a lengthening of their decay time when comparing with the



Fig. 6 Excitation spectra of L1, C1 and C'1 in acetonitrile, emission spectra of C1 (acetonitrile).

value reported for [Ru(Phen)₃](PF₆)₂ (Table 1). Interestingly, each addition of three fluorenes going from $[Ru(Phen)_3](PF_6)_2$ to C2, increases the lifetime of the complex by approximately 0.8 µs. This trend has already been observed in similar complexes involving the pyrene unit and ascribed to a thermal equilibration between the lowest-lying triplet states located at the two electronicallydistinct subunits.²¹ C'1 presents an emission band centered at 480 nm (Table 1 and Fig. 2) excited only in intraligand states, no information could be obtained for C'2, probably due to the lability of the complex at the low concentrations used for luminescence measurements, since in this case, only the fluorescence of the ligand L2 was observed. Complexation by zinc induces a large shift of 80 nm of the ILCT emission band with respect to that of L1. Although the Zn complexation leads to a lengthening of the decay time of the fluorescence, it keeps the same order of magnitude (6.1 ns) than that of L1 (1.4 ns), in good agreement with a singlet state emission.

Two-photon excitation spectra of L1, L2, Zn complex C'1 and Ru complexes C1 and C2 are displayed in Fig. 7 and Fig. 8, respectively. Ligands L1 and L2 present a wide TPA band at 530 (16 GM) and 560 (75 GM) nm. Although these TPA maxima are close to half wavelength linear absorptions (270



Fig. 7 Two-photon excitation spectra of L1, L2, and C1 measured in acetonitrile (the experimental uncertainty for two-photon measurements is $\pm 15\%$). For comparison, linear excitation spectrum of C1 was also reported.



Fig. 8 Two-photon excitation spectra of C1, C2, Ru(Phen)₃²⁺ measured in acetonitrile (the experimental uncertainty is $\pm 15\%$). For comparison, linear excitation spectrum of C2 was also reported.

and 265 nm, respectively), which was shown above to involve only the phenanthroline moiety, the width of these bands allows to assume the existence of several transitions. Theoretical TPA properties of L2 confirms the existence of two transitions at 520 and 488 nm (Table 1); these transitions involve configurations between molecular orbitals centered on the phenanthroline itself and CT type configurations. The partial CT character of these transitions is in good agreement with the experimental intensity increase and bathochromic shift of these bands from L1 to L2. It is worth noting that TPA spectra do not match linear absorption in spite of the non-centrosymmetry of these systems in which one-photon absorption transitions are also allowed in TPA, since one-photon absorption transitions at 310 (for L1) and 340 nm (for L2) were not detected in TPA spectra at 620 and 680 nm, respectively. The weak efficiency of the 1,10-phenanthroline as an acceptor group, may be responsible for this behavior.

A TPA band is observed at 595 nm for C'1, with a crosssection σ_{TPA} of 90 GM, the matching between one- and twophoton absorption spectra (see Fig. 7), is in agreement with the octupolar structure of these complexes. As for C'1, below 560 nm and due to position of their emission band, spectra could not be registered in the 470–650 nm wavelength range for Ru complexes. In the 700–950 nm range, two TPA bands at 750 and 850–930 nm were observed for C1 and C2 (Fig. 8). As previously mentioned for C'1, most of these bands can be superimposed with those of linear excitation spectra. The antenna effect²² induced transition at 750 nm, presents an enhanced efficiency from C1 to C2 (40 to 90 GM, respectively, see Table 1), due to the ligand substitution with an additional fluorene unit.

The near-IR maxima σ_{TPA} value at 850 and 930 nm (~15 GM for both complexes and [Ru(Phen)_3](PF_6)_2) does not depend on the ligand. This transition corresponds to the MLCT band, and its spectral distribution is observed here for the first time in Ru complexes by two-photon excitation. The origin of this band is confirmed from Zn complexes spectra, in which no absorption was observed in the same wavelength range.

Conclusions

In conclusion, we have presented herein two new fluorenesubstituted 1,10-phenanthroline ligands and the preparation and photophysical properties of related octupolar zinc and ruthenium(II) complexes. The possibility to tune the excited-state lifetime or the absorption spectral range has been demonstrated. This paper contributes to show the great interest of Ru and Zn complexes for TPA based effects, in both complexes, TPA intraligand charge transfer bands were observed with an enhanced efficiency. In that context, synthesis of longer fluorene chains is in progress to complete the series. For the first time in Ru coordination complexes, detection of the MLCT band led to a TPA spectral enlargement (500-900 nm) with respect to that of related ligands. The longer luminescence decay times in these complexes (several ns and µs in Zn and Ru systems, respectively) with respect to these ligands could be in favor of excited state reabsorption, which could lead to optimize optical limiting phenomenon induced by TPA. Furthermore and as far as reactivity and luminescence properties are concerned, access to the long lived triplet ³MLCT excited state by TPA (in the 700-1000 nm spectral range), opens up the way to applications such as photodecomposition of water,23 molecular switches,24 DNA recognition and binding²⁵ or time and spatial resolved O₂ sensors,²⁶ including in living cells.13 These two last points are currently being studied in the group and will be reported in a forthcoming article.

Experimental

Syntheses

Thin-layer chromatography was carried out on Merck Kieselgel $60F_{254}$ precoated on alumina silica gel plates. Preparative flash chromatography was performed on Merck Gerduran 60. ¹H and ¹³C NMR spectra were recorded on a Bruker DPX 200 spectrometer (at 200.13 MHz for ¹H and 50.32 MHz for ¹³C) and also on a Varian Unity Plus at 499.84 MHz for ¹H. Elemental analysis were carried out by the Service Central d'Analyse, CNRS. UV/Vis spectra were recorded in the 200–800 nm range on a UV/Vis Jasco V-550; λ_{max} are given in nm and molar extinction coefficients ε in L mol⁻¹ cm⁻¹. Melting temperatures (mp) were measured on a Perkin-Elmer DSC7 micro-calorimeter.

Preparation of ligands L1 and L2

Typical procedure for L1. In a 250 mL round bottom flask under inert atmosphere, boronic acid 2 (4.5 g, 11.9 mmol) and 5bromo-1,10-phenanthroline 1 (3.08 g, 11.9 mmol) were dissolved in a mixture of 60 mL toluene and 60 mL of a 1 M Na₂CO₃ aqueous solution. After addition of catalyst Pd(PPh₃)₄ (412 mg, 0.36 mmol, 3%), the reaction mixture was refluxed under stirring for 3 d. Yield: 60%; mp: 121 °C. ¹H NMR (499.84 Hz, 300 K, CD_2Cl_2) 9.20 (2H, m, H₂, H₉), 8.40–8.34 (2H, m, ${}^{3}J = 8$ Hz, ${}^{5}J =$ 1.5 Hz, H₄, H₇), 7.94-7.92 (1H, m, H₁₂), 7.89 (1H, s, H₆), 7.86-7.82 (1H, m, H₁₃), 7.72 (1H, m, H₃), 7.62 (1H, m, H₈), 7.57 (1H, s, H₁₇), 7.55 (1H, d, H₁₁), 7.48–7.39 (3H, m, H₁₄, H₁₅, H₁₆), 2.08 (4H, m, H_{alkyl}), 1.19–1.10 (12H, m, H_{alkyl}), 0.83–0.75 (10H, m, H_{alkyl}). ¹³C NMR (50.32 MHz, 300 K, CDCl₃) 150.9, 150.8, 149.9, 149.8, 146.4, 145.6, 140.9, 140.3, 139.2, 137.2, 135.7, 134.4, 128.5, 128.0, 127.3, 126.8, 126.2, 124.3, 123.2, 122.8, 122.5, 119.8, 119.7, 55.1, 40.1, 31.3, 29.5, 23.7, 22.4, 13.8. Anal. Calcd for C₃₇H₄₀N₂·0.5H₂O: C, 85.17; H, 7.92. Found: C, 85.13; H, 8.01%. UV-vis (CHCl₃) λ_{max} $(\varepsilon) = 312 (21400); 272 (35000); 240 (21200); 217 (18900).$

L2. Yield: 67%; mp: 128 °C. ¹H NMR (499.84 Hz, 300 K, CDCl₃) 9.21 (2H, m, H₂, H₉), 8.35–8.33 (1H, m, ${}^{3}J = 8$ Hz, ${}^{5}J = 1.5$ Hz, H₃ or H₈), 8.30–8.28 (1H, m, ${}^{3}J = 8$ Hz, ${}^{5}J = 1.5$ Hz, H₈ or H₃), 7.98–7.48 (13H, m), 7,36–7.29 (3H, m, H₁₈, H₁₉, H₂₀), 2.08–2.00 (8H, m, H_{alkyl}), 1.15–1.03 (24H, m, H_{alkyl}), 0.82–0.69 (20H, m, H_{alkyl}). ¹³C NMR (50.32 MHz, 300 K, CDCl₃) 151.70, 151.49, 151.41, 150.97, 150.04, 141.00, 140.80, 140.71, 140.44, 140.30, 139.63, 139.41, 137.40, 135.90, 128.80, 128.16, 126.79, 126.37, 126.28, 126.05, 124.57, 123.36, 122.91, 122.72, 121.51, 121.40, 120.15, 119.89, 119.72, 55.39, 55.16, 40.35, 40.28, 31.45, 29.66, 29.61, 29.25, 23.90, 22.52, 14.00, 13.98. Anal. Calcd for C₆₂H₇₂N₂·0.3H₂O: C, 87.72; N, 3.29%. Found: C, 87.66; N, 3.29%. UV-vis (CHCl₃) λ_{max} (ε) = 341 (61400); 268 (28900); 242 (36600); 213 (23100).

Preparation of complexes C1, C2, C'1 and C'2

Ruthenium and zinc complexes were obtained by reaction under reflux of three equivalents of ligand (L1 and L2 for C1, C'1 and, C2, C'2, respectively) with one equivalent of ruthenium trichloride (in dimethylformamide) and zinc acetate (in ethanol) for C1, C2 and C'1, C'2, respectively and precipited by NH_4PF_6 .

Typical procedure for C1: a DMF solution of 600 mg of compound L1 (1.17 mmol) was dropwise added, under argon, to 100 mg of RuCl₃·3H₂O (0.38 mmol) dissolved in DMF and refluxed for a night. Saturated aqueous solution of NH₄PF₆ was then added to the resulting solution at room temperature. 556 mg of a red precipitate was collected by filtration, washed three times with H₂O and twice with pentane. Dissolved in dichloromethane, the resulting solution was dried over Na₂SO₄ After filtration and evaporation, the desired complex was recristallized in absolute ethanol to yield 410 mg of a red solid (white solid for zinc complexes). Yield: 79%; mp: not found (20-450 °C). ¹H NMR (499.84 MHz, CD₂Cl₂) δ 8.62 (2H, m, H₄, H₇), 8.35-8.17 (3H, m, H₂, H₆, H₉), 7.99 (1H, m, H₁₂), 7.89-7.84 (2H, m, H₁₃, H₃ or H_8), 7.57 (1H, m, H_8 or H_3), 7.65 (2H, m, H_{11} , H_{17}), 7.44 (3H, m, H₁₄, H₁₅, H₁₆), 2.09 (4H, m, H_{alkyl}), 1.13 (12H, m, H_{alkyl}), 0.82-0.75 (10H, m, H_{alkyl}). Anal. Calcd. for $RuC_{111}H_{120}N_6P_2F_{12}\cdot H_2O$: C, 68.47; H, 4.32; N, 4.32. Found: C, 68.44; H, 4.38; N, 4.38%. UV-vis (CHCl₃): λ_{max} (ε) = 452(29900); 422(28100); 345(42600); 308(48900); 270(125500); 216(52600). ESI-HRMS Calcd for RuC₁₁₁H₁₂₀N₆PF₆: 1783.82543 M⁺, exp: 1783.83670.

C'1. Yield: 61%; mp: 401 °C; ¹H NMR (499.84 MHz, CDCl₃) 8.77–8.46 (4H, m, H₂, H₃, H₈, H₉), 8.14–8.06 (2H, m, H₆, H₄ or H₇), 8.02–8.79 (2H, m, H₄ or H₇, H₁₂), 7.84–7.82 (1H, m, H₁₃), 7.57–7.52 (2H, m, H₁₁, H₁₇), 7.42 (3H, m, H₁₄, H₁₅, H₁₆), 2.07– 2.05 (4H, m, H_{alkyl}), 1.15–1.06 (12H, m, H_{alkyl}), 0.82–0.75 (10H, m, H_{alkyl}). Anal. Calcd. for ZnC₁₁₁H₁₂₀N₆P₂F₁₂·2H₂O: C, 69.09; H, 6.47; N, 4.35; Zn, 3.38. Found: C, 68.97; H, 6.42; N, 4.48; Zn, 3.59%. UV-vis (CHCl₃) λ_{max} (ε) = 340 (40000); 273 (137500); 241 (55300); 218 (52700).

C2. Yield: 60%; mp: not found (20–450 °C). ¹H NMR (499.84 Hz, 300 K, CD₂Cl₂) 8.64–8.62 (2H, m, H₄, H₇), 8.47–8.25 (4H, m, H₂, H₃, H₈, H₉), 8.04–8.25 (11H, m), 7.45–7.36 (3H, m, H₁₈, H₁₉, H₂₀), 2.19–1.76 (8H, m, H_{alkyl}), 1.16 (24H, m, H_{alkyl}), 0.82–0.75 (20H, m, H_{alkyl}). Anal. Calcd. for RuC₁₈₆H₂₁₆N₆P₂F₁₂: C, 76.33; H, 7.43; N, 2.87. Found: C, 76.30; H, 7.97; N, 3.02%. UV-vis (CHCl₃) : λ_{max} (ε) = 459(27100); 334(145200);

267(101900); 243(92700); 215(75900). HRMS(MALDI): Calcd for RuC₁₈₆H₂₁₆N₆: 2635.60194 M⁺; Exp. : 2635.61245.

C'2. Yield: 76%; mp: not found (20–450 °C). ¹H NMR (499.84 Hz, 300 K, CD₂Cl₂) 8.85–8.79 (2H, m, H₂, H₉), 8.6–8.4 (2H, m), 8.25–8.22 (1H, m), 8.06–7.62 (12H, m), 7.43–7.38 (3H, m, H₁₈, H₁₉, H₂₀), 2.19–2.09 (8H, m, H_{alkyl}), 1.16 (24H, m, H_{alkyl}), 0.82–0.73 (20H, m, H_{alkyl}). Anal. Calcd. for ZnC₁₈₆H₂₁₆N₆P₂F₁₂·4H₂O: C, 75.39; H, 7.60; N, 2.80. Found: C, 75.35; H, 7.64; N, 3.11%. UV-vis (CHCl₃) λ_{max} (ε) = 335(145300); 301(92600); 275(91100); 243(86000); 214(63900).

Physical measurements

Luminescence. The steady-state emission spectra were recorded on a Photon Technology International (PTI) SE-900M spectrofluorimeter. All the samples were prepared in a glovebox in deoxygenated CH₃CN and contained in 1 cm quartz cell. The samples were maintained in aerobic conditions with a Teflon cap. Emission quantum yield $\phi_{\rm L}$ were determined at 25 °C in deoxygenated acetonitrile solutions with a CH₃CN solution of [Ru^{II}(phen)₃](PF₆)₂ ($\phi_{\rm L}^{\rm Ref} = 0.03$) as a standard, according to eqn (1),

$$\phi_{\rm L}^{\rm S} = \frac{I_{\rm L}^{\rm S}}{I_{\rm L}^{\rm Ref}} \frac{\left(1 - 10^{-\rm OD^{\rm Ref}}\right)}{\left(1 - 10^{-\rm OD^{\rm S}}\right)} \phi_{\rm L}^{\rm Ref} \tag{1}$$

where $I_{\rm L}$, the emission intensity, was calculated from the spectrum area $\int I(\lambda) d\lambda$ and OD represents the optical density at the excitation wavelength. The superscripts "S" and "Ref" refer to the sample and the standard, respectively. The luminescence lifetime measurements for the complexes C1 and C2 were performed after irradiation at $\lambda = 337$ nm obtained with a 4 ns pulsed N₂ laser (optilas VSL-337ND-S) and recorded at the emission maximum wavelength using a monochromator and a photomultiplicator tube (Hamamatsu R928) coupled with an ultra-fast oscilloscope (Tektronix TDS 520A). Fluorescence decay measurements of the ligands L1 and L2 were performed after irradiation at λ_{exc} = 400 nm obtained by the second harmonic of a Titanium : Saphire laser (picosecond Tsunami laser spectra physics 3950-MIBB) at a 8 MHz repetition rate. The Fluotime 200 from AMS technologies is used for decay acquisition. It consists of a GaAs microchannel plate photomultiplier tube (Hamamatsu model R3809U-50) followed by a time-correlated single photon counting system from picoquant (PicoHarp300).

Nonlinear optical measurements. The TPEF technique was used to measure the two-photon absorption cross-section σ_{TPA} using a femtosecond Ti-sapphire laser and a nanosecond OPO pumped by tripled Nd:YAG laser as excitation sources in the 700–950 and 450–650 nm ranges, respectively (spectral range 650–700 nm is inaccessible with our experimental set-up). The TPA experimental set-up has already been described.²⁷ TPA excitation spectra were recorded from fluorescence detected by a fiber optic CCD spectrometer and collected at 90° of the incident. The TPA cross-section was determined from 2×10^{-3} mol L⁻¹ solutions in acetonitrile of molecules, using the reference TPA cross-section of 210 GM (GM for Göppert–Mayer unit, 1 GM = 10^{-50} cm⁴ photon⁻¹ s⁻¹) at 840 nm for Rhodamine B in methanol as reported in Table 2 of ref. 28 in order to scale two-photon excited fluorescence spectra and the pulse energy was kept low enough

to ensure a quadratic dependence of the fluorescence signal on input energy. For each of our compound, fluorescence efficiencies, including the concentration dependent self-quenching, were taken into account by comparison with the one-photon fluorescence that was obtained at visible wavelengths in the same excitation and collection geometry.

Calculations

Semi-empirical quantum chemistry calculations were used, following the method described in ref. 14*a*, to analyse one- and two-photon absorption spectra. The geometry of molecules was optimized in the ground state by CACHE.²⁹

Acknowledgements

The authors thank J. Bernard for technical assistance and Direction Générale de l'Armement for financial support.

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